THE THERMODYNAMICS OF DILUTE INTERSTITIAL
SOLID SOLUTIONS

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A. INTRODUCTION

In analyzing experimental thermodynamic data for solid
solutions it is convenient to classify the solutions into two cate-
gories; in one category we deal with solutions in which the inter-
action between solute atoms manifests itself in a non-random solute
atom distribution and the second category is a special case of the
first where the solution is dilute enough to enable solute-solute
interactions to be ignored and the solute atom distribution is ran-
dom. In the general category of solutions the partial energy of
solution $\overline{E}_u$ is a function of composition and the partial entropy $\overline{S}_u$
is non-ideal. In the second class of solution, which may be termed
quasi-regular, $\overline{E}_u$ is not dependent on the solute concentration and
although the entropy may be non-ideal the configurational contribu-
tion to the partial entropy is ideal and thus easily calculated.
From an experimental point of view we can say that a solution is
quasi-regular when it is dilute enough for the solute to obey Henry's
law.

Most of the statistical theories of solutions assume that
the state sum Ω_i due to the internal degrees of freedom (terms due to
vibrational, magnetic, or electronic specific heat changes) is separable
from the configurational state sum Ω_c so that the state sum Ω for the
whole solution can be written,

$$\Omega = \Omega_i \sum_c g(E_c) \ e^{-E_c/kT} \tag{1}$$

where $g(E_c)$ denotes the number of non-degenerate states in the configu-
ration of energy E_c. The evaluation of the combinatorial factor $g(E_c)$

in equation (1) is simple for a chain of atoms and the calculation
for a two-dimensional lattice (Ising model) can be carried out when
the problem is formulated in an appropriate matrix notation[1]. How-
ever, the exact evaluation of $g(E_c)$ for a three-dimensional lattice
meets with great mathematical difficulty and has not yet been accomplished.
Much of statistical solution theory consists of attempts to estimate
the thermodynamic parameters of solutions by making approximations for
$g(E_c)$ in equation (1).

The simplest approximation is the zero-order Bragg and Williams[2]
approximation in which $g(E_c)$ is replaced by a term corresponding to random
mixing in spite of the fact that the energetics of the solution are non-
ideal. A better approximation is the quasi-chemical model[3] in which
the energy of solution is characterized by pairwise interaction energies
which are assumed to be independent of composition. The number of con-
figurations corresponding to a given energy is found by counting the
possible orientations of each pair in the lattice. If the degree of
short-range-order in a solution is determined, the excess thermodynamic
functions can be calculated from the quasi-chemical model. For a few
metallic solid solutions (concentrated Cu-Au alloys) the model is remark-
ably successful but in general agreement is poor[4]. It is to be noted
that both the Bragg-Williams and the quasi-chemical models do not take
non-configurational entropy changes into account.

Because of the incomplete state of the statistical interaction
theories the interpretation of experimental thermodynamic data on concentrated
solutions is subject to more limitations than the analysis of data for
quasi-regular solutions. In these latter solutions the combinatorial

factor $g(E_c)$ reduces to its value in an ideal solution and the solid

solution crystal is characterized by a single interaction energy. Thus

the state sum and the chemical potential of a solute atom can be written

down explicitly. The chemical potential μ_u^S of a solute atom in a quasi-

regular solution is given by[5]

$$\mu_u^S = \overline{E}_u - T\overline{S}_u^V + kT \ \ln \ \frac{\theta/\beta}{1 - \theta/\beta} \tag{2}$$

where θ is the ratio of the numbers of solute atoms to solvent atoms, β

is the number of interstices of a given kind per lattice atom and $\overline{E}_u$ is

the energy required to insert a solute atom into the solution measured

with respect to the energy of an atom at rest in a vacuum. The term

$\overline{S}_u^V$ is the partial excess entropy of a solute atom,

$$\overline{S}_u^V = \lim_{C_u \to 0} \left(\frac{\partial S}{\partial N_u}\right)_V + k \ \ln \ \frac{\theta/\beta}{1 - \theta/\beta} \tag{3}$$

where S is the total entropy of the solution. Throughout v is used

to denote solvent and u to denote solute.

Equation (2) can be used in the analysis of solubility data

for quasi-regular solutions and the parameters found are important in

the development of the theory of interstitial solid solutions. The

energy $\overline{E}_u$ can be used to check fundamental quantum mechanical calculations

for the case when the interaction energy is not complicated by solute-

solute terms. Furthermore since the partial configurational entropy

$- k \ \ln \ \theta/\beta/(1 - \theta/\beta)$ is known explicitly, analysis of the solubility

data yields $\overline{S}_u^V$, the non-configurational partial entropy. For solutions

where no magnetic or electronic specific heat changes occur this excess

partial entropy can be interpreted as a vibrational entropy due to the

perturbation of the normal modes of the solvent lattice which occurs when a solute atom is inserted. The parameters $\bar{E}_u$ and $\bar{S}_u^V$ are also useful in the development of theories for concentrated solutions since the partial energies and entropies in concentrated solutions must approach $\bar{E}_u$ and $\bar{S}_u^V$ in the limit as the solute concentration approaches low values.

This report will present a review of some of the models used to represent quasi-regular interstitial solid solutions together with a discussion of the applications of the models to the analysis of data for the variation of the solute solubility with temperature. Instead of attempting a general approach the discussion will be limited to a consideration of two groups of interstitial solutions - nitrogen and carbon dissolved in iron, and hydrogen alloys.

The solutions and models discussed are in thermodynamic equilibrium with a second phase. The solvent lattice is "perfect" in that it does not contain defects such as vacancies or dislocations at a concentration which would provide low energy sites where solute atoms could locate and give rise to a measurable deviation from the normal lattice solubility.

B. IRON-BASED INTERSTITIAL SOLID SOLUTIONS

The iron-carbon system is one of the most intensively studied binary systems. Much data exists on the equilibrium of dilute solid solutions of carbon in both α and γ-iron with a second phase, both when the second phase is a solid or liquid (equilibrium diagram work) and when the second phase is gaseous. If the thermodynamic functions of the C-atoms in the second phase are known then experimental data for the variation of the equilibrium with temperature can be analyzed to give the thermodynamic parameters of the C-atoms dissolved in the solid.

Smith[6] and Dünwald and Wagner[7] have measured the equilibrium between ferrite and austenite and mixtures of $CO + CO_2$ and $H_2 + CH_4$ at several temperatures and more recently Ellis, Davidson, and Bodsworth[8] determined the equilibrium between austenite and a gas containing CH_4, H_2, CO_2, CO and H_2O at two temperatures. In the experiments of Smith and Dünwald and Wagner the variation in the ratios $r_1 = P_{CH_4}/P_{H_2}^2$ and $r_2 = P_{CO}^2/P_{CO_2}$ with the C-content in ferrite and austenite was measured. From a knowledge of the equilibrium constants for the reactions:

$$2H_2 \ (g) + C \ (gr) \rightarrow CH_4 \ (g)$$

$$CO_2 \ (g) + C \ (gr) \rightarrow 2CO \ (g)$$
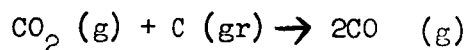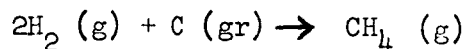
the activity a_c of the carbon in solution relative to graphite (gr) can be calculated from the measurements of r_1 and r_2. It was found in both sets of experiments that the C-atoms in ferrite (at 750° C and 800° C) obey Henry's law up to the limit where the $\alpha \rightarrow \gamma$ transition occurs. The austenite equilibrium was measured at 1000, 1070 and 1200° C and it is found that the solute obeys Henry's law up to about 1 → 2 At% but at higher C-contents there is a marked departure and the C-activity increases

with C-content more rapidly than Henry's law would predict.

Let us first give a brief discussion of the models which have been considered to explain the deviation from Henry's law in the more concentrated austenite and then proceed to a discussion of the very dilute solutions.

Darken and Smith[9] considered a simple statistical model in which a C-atom in its octahedral site in the F.C.C. lattice has either one or no neighboring C-atoms in the 12 nearest neighbor octahedral sites. This model thus contains two characteristic interaction energies since it is assumed that the number of C-atoms having more than one nearest neighbor C-atom is negligible and a solute atom does not interact with another solute atom situated at greater distance than the first shell of interstitial sites. Darken and Smith showed that this model gives reasonable agreement with the measured variation in the activity of C with composition. It is interesting to note that Darken and Smith concluded from the analysis of the data in the light of their model that there was a slight repulsive force between C-atoms in austenite which reduces the concentration of C-C pairs below that which corresponds to random mixing.

The exclusion of solute atoms from nearest neighbor sites in an interstitial solution has been a basic postulate in other models used to explain the C-activity data in austenite. This "blocking" was formulated by Speiser and Spretnak[10] who considered that an integral number z of sites could be blocked by a solute atom. The molar configurational entropy of such a solution in terms of c_u, the atom fraction of solute, is given by[5]

$$S_z^c = -\frac{R}{z}\left\{c_u \, z \, \ln\left(\frac{c_u}{\beta}\right) - \beta(1-c_u)\ln(1-c_u)\right.$$
$$\left. + \beta\left(1 - \frac{c_u(\beta+z)}{\beta}\right)\ln\left(1 - \frac{c_u(\beta+z)}{\beta}\right)\right\} \qquad (4)$$

For a perfectly random solution (no blocking) $z = 1$ and putting $z = 1$ in Equation (4) gives the configurational entropy of a random interstitial solution S^c.

$$S^c = -R\left\{c_u \ln\frac{c_u}{\beta} - \beta(1-c_u)\ln(1-c_u)\right.$$
$$\left. + \beta\left(1 - \frac{c_u(\beta+1)}{\beta}\right)\ln\left(1 - \frac{c_u(\beta+1)}{\beta}\right)\right\} \qquad (5)$$

A plot of these two functions for $z = 5$ is shown in Fig. (1). The entropy curve for the blocked solution does not differ sensibly from that of the random solution until c_u is about 2.0 At%.

It has been customary to describe the thermodynamics of interstitial solutions in terms of the variation in activity a_c with solute content and, in parallel to the treatment of substitutional solutions, to define a_c by an equation of the type,

$$\mu_u^s = \mu_u^o + kT \ln a_u \qquad (6)$$

using the pure solute as a reference material (graphite in the case of Fe-C solutions). However, it can be seen from equation (2) that for an ideal interstitial solution

$$\mu_u^s = \mu_u^o + kT \ln \frac{c_u}{1 - 2c_u} \qquad (7)$$

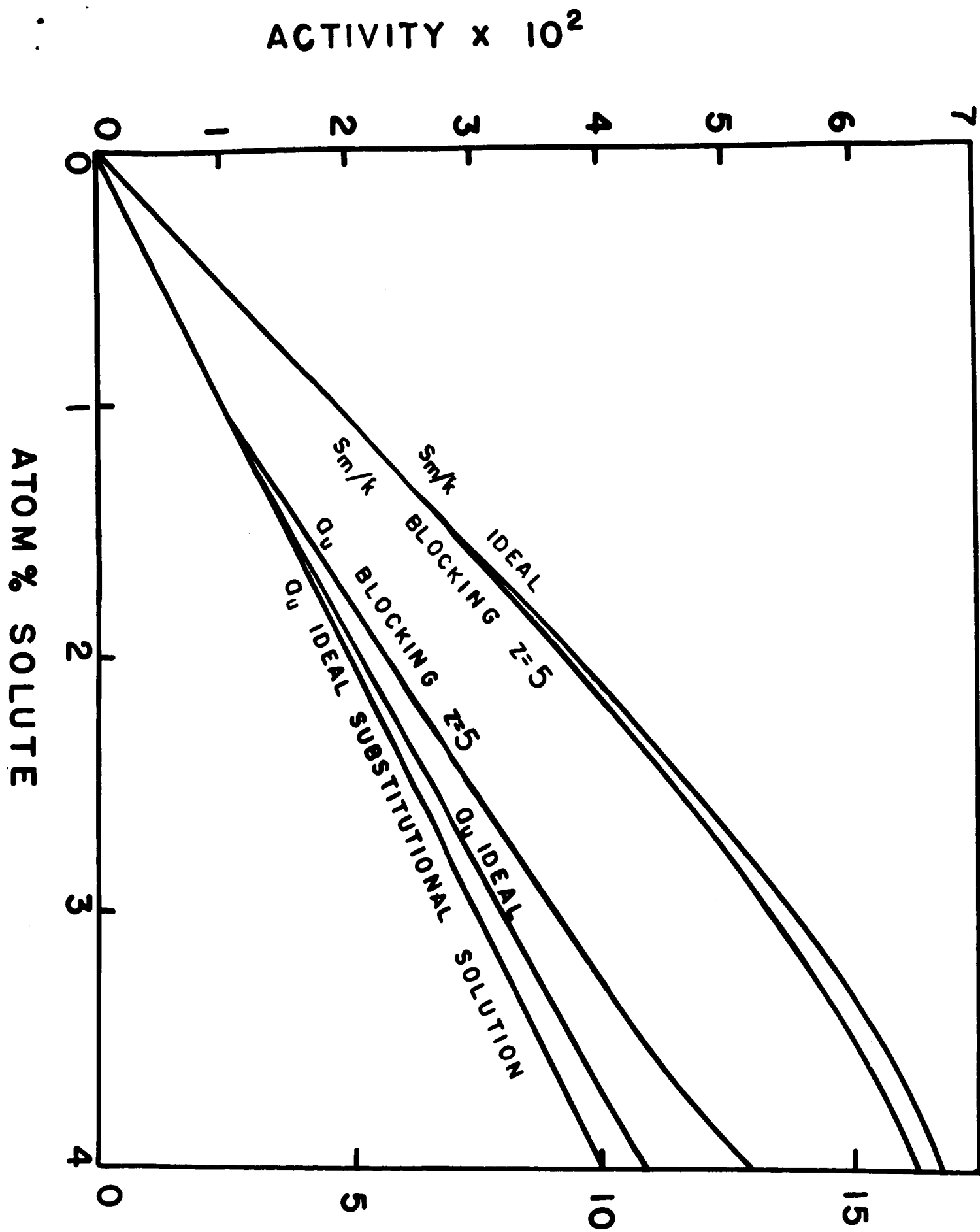where, for simplicity we have put $\beta = 1$. Thus even for an ideal inter-

Fig. 1

stitial solution the activity defined in equation (6) is not equal

to the atom fraction of solute and a_u is not proportional to c_u in

a quasi-regular solution. Fig. (1) shows the activity vs composi-

tion curve for an ideal solution and it can be seen that at solute

compositions greater than about 2 At% there is a sensible departure

from linearity. In a **rigorous** discussion of interstitial solid

solutions Henry's law should be restated or the activity should be

defined by an equation of the form

$$\mu_u^s = \mu_u^o + kT \ln \frac{a_u'}{1-2\,a_u'} \quad . \tag{8}$$

It can be shown[5] that the chemical potential of a blocked solu-

tion is given by

$$\mu_u^{s'} = \overline{E}_u - T\overline{S}_u^v + kT \ln \frac{\theta/\beta}{1-\theta z/\beta} \quad . \tag{9}$$

Thus if $\overline{E}_u$ and $\overline{S}_u^v$ are independent of composition then the composi-

tion dependence of the activity at a given temperature is determined

by the expression

$$\frac{\theta/\beta}{1-\theta z/\beta} = \frac{c_u}{1-c_u(z+1)} \tag{10}$$

where $\beta = 1$. A plot of this function for $z = 5$ is shown in fig. 1.

It can be seen that there is a strong departure of this function from

plot for an ideal solution. The departure becomes experimentally signifi-

cant between $c_u = 0.01$ and 0.015.

Many models have been set up to explain the thermodynamic be-

havior of c in γ-iron in which it is assumed that although blocking is

present and the configurational entropy is non-random the partial energy and partial non-configurational entropy are independent of solute content (as in equation (9)). Scheil[11][12] and Kaufman, Radcliffe, and Cohen[13] have analyzed the data of Smith and deduced that $z = 5$ from the solute activity data. On the other hand Schwarzmann and Temkin[14] deduced that a C-atom blocks only three other interstitial sites so that $z = 4$. Ellis, Davidson, and Bodsworth[8] determined the variation in a_c with C-content in austenite at 925° C and 1050° C. At both temperatures a_c began to deviate from Henry's law at between $c_u = 0.03$ and 0.04. The authors concluded from the analysis of their data that $z = 4$.

Let us now turn to a consideration of the Fe-C solutions which are dilute enough to obey Henry's laws. McLellan[15] has analyzed the data of Smith and Dünwald and Wagner for the equilibrium of CO-CO$_2$ and CH$_4$ - H$_2$ mixtures with ferrite and austenite, utilizing only the data for equilibriums in the range where the C-activity (as measured by r_1 and r_2) varies linearly with C-content. Suitable equilibrium determinations were made at 750° C and 800° C for ferrite and 940° C, 1000° C, 1070° C, and 1200° C for austenite. In this work it was assumed that the solid solutions were quasi-regular so that the chemical potential of a solute atom in solution is given by equation (2). This chemical potential was then equated to that of C-atoms in the gas, enabling a solubility equation to be deduced. The theoretical solubility equation was used to extract the relevant thermodynamic parameters of the solid solutions from the experimental equilibrium data.

The solubility equation deduced for the $CH_4 - H_2$ equilibriums is,

$$\frac{\theta/\beta}{1-\theta/\beta} = \frac{r_1 kT^3 \phi}{Z^v_{CH_4}} e\left[\bar{E}_u - \left(E^o_{CH_4} - 2E^o_{H_2}\right)\right]/kT \; e^{\bar{S}^v_u/k} \tag{10}$$

where $\phi = \left\{\frac{(2\pi 2m_H k)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_{H_2} k}{2h^2}\right\}^2 \Big/ \left\{\frac{(2\pi m_{CH_4} k)^{3/2}}{h^3} \cdot\right.$

$$\left. \cdot \frac{8\pi^2(2\pi I_{CH_4} k)^{3/2}}{12h^3}\right\} \tag{11}$$

and for the $CO_2 - CO$ equilibriums

$$\frac{\theta/\beta}{1-\theta/\beta} = \frac{r_2 \Psi}{kT^{7/4}} \cdot \frac{Z^v_{CO_2}}{\left(Z^v_{CO}\right)^2} e\left[\bar{E}_u + \left(E^o_{CO_2} - 2E^o_{CO}\right)\right]/kT \; e^{\bar{S}^v_u/k} \tag{12}$$

where

$$\Psi = \left\{\frac{(2\pi m_{CO} k)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_{CO_2} k}{2h^2}\right\} \Big/ \left\{\frac{(2\pi m_{CO} k)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_{CO} k}{h^2}\right\}^2 \cdot \tag{13}$$

In these equations Z denotes the vibrational state sum of the molecules in the gas, I their moments of inertia, m their mass, and $-E^o$ is the dissociation energy at $0°$ K. These solubility equations take the complex temperature dependence of the chemical potential of solute atoms in the gas explicitly into account and enable reliable values of $\bar{E}_u$ and $\bar{S}^v_u$ to be obtained from the experimentally determined variation in θ with r_1 and r_2 at different temperatures.

A similar analysis has been applied to the solubility data for nitrogen in ferrite and austenite in equilibrium with N_2 gas.[5] The solubility of N in an interstitial solution in equilibrium with N_2 molecules is

$$\frac{\theta/\beta}{1-\theta/\beta} = \frac{P_{N_2}^{1/2}\,\lambda}{T^{7/4}\left(Z_{N_2}^{v}\right)^{1/2}}\;e^{-(\bar{E}_u - \frac{1}{2}E_{N_2}^{o})/kT}\;e^{\bar{S}_u^{v}/k} \qquad (14)$$

where $\lambda = \left\{\dfrac{h^3}{(2\pi 2 m_N k)^{3/2}} \cdot \dfrac{2h^2}{8\pi^2 I_{N_2} k} \cdot \dfrac{1}{k}\right\}^{1/2}$ \qquad (15)

where P_{N_2} is the partial pressure of N_2 molecules. This equation was used to estimate the values of $\bar{E}_u$ and $\bar{S}_u^v$ from the experimental solubility data.

The thermodynamic data obtained from these analyses are given in Table 1 .

<p style="text-align:center"><u>TABLE 1.</u></p>

Solution	$\bar{E}_u$ k.cal/mole	$\bar{S}_u^v/k$
C - α Fe	-147.2	5.20
C - γ Fe	-155.2	5.75
N - α Fe	- 74.3	7.20
N - γ Fe	- 81.9	6.20

The equilibrium data of Ellis, Davidson, and Bodsworth[8] have not been analyzed by this technique but estimates of $\bar{E}_u$ and $\bar{S}_u^v$ can be obtained from their published activity data from the equation

$$\frac{c_u}{1-2c_u} = a_u\,e^{-\Delta\bar{H}_u/kT}\;e^{(\bar{S}_u^v - S_u^o)/k} \qquad (16)$$

where $\Delta\bar{H}_u \equiv \bar{H}_u - H_u^o$ is the relative partial molar enthalpy of a solute atom and S_u^o is the standard entropy of the pure solute (graphite). The value of $\Delta\bar{H}_u$ deduced obtained from the data is 11.57 k. cal/mole and this is presumably a mean value for the two temperatures at which the activity was measured. Using enthalpy tables[16] to obtain H_u^o the

value of $\bar{E}_u$ is -154.5 k. cals/mole in good agreement with value given in Table $\underline{1}$. The value of $\bar{S}_u^V$ estimated from $(\bar{S}_u^V - S_u^o)$ and tables of standard entropies[16] is 5.77 k.

The advantage of deducing the thermodynamic parameters of a solution from solubility data with a closed solubility equation is that it obviates the use of a reference state and the partial entropy can be obtained without recourse to extra data on the equilibrium of the gas phase with graphite. Moreover, the analysis is carried out in terms of equations which are easily understood physically.

The data of Table $\underline{1}$ was obtained using the assumption that solute atoms occupy only one kind of interstitial site. Recently[17] it has been shown that if the C-atoms in α-iron can occupy both the octahedral and tetrahedral sites, the deviation from linearity at high temperatures of an Arhenius plot of the diffusivity of C through α-iron could be explained. The thermodynamic functions of a solution with dual site occupancy will differ from those of a quasi-regular solution in which only one kind of site is occupied. The differences in partial energy, entropy, and Gibbs potential between a dual occupancy solution and a single occupancy solution of the same composition are given by

$$\Delta \tilde{E}_u = \Delta E (1 - \delta) \tag{16}$$

$$\Delta \tilde{S}_u = \frac{\Delta E}{T} (1 - \delta) - k \ln \delta \tag{17}$$

$$\Delta \tilde{u}_u = kT \ln \delta \tag{18}$$

where δ is the fraction of solute atoms located at octahedral sites. The analysis of the diffusion data using this model indicated that at

800° C only one solute atom in 1000 is located at a tetrahedral site and thus no effect of their presence on the measured thermodynamic parameters should be seen. They have a measurable effect on the diffusivity at high temperatures since the diffusion rate via tetrahedral sites is relatively large.

The information table $\underline{1}$ represents reliable data for the thermodynamics of quasi-regular Fe-C and Fe-N solutions. A brief discussion of the partial energies and entropies has been given[15] and it was shown that for both N and C solutes electronic specific heat and magnetic spin changes were probably negligible and $\overline{S}_u^v$ arises from vibrational changes.

C. HYDROGEN-METAL SOLUTIONS

In this section the experimental solubility data for hydrogen-metal solutions are presented, previous models for hydrogen alloys are briefly discussed, and finally the data are analyzed by assuming a quasi-regular solution model for the solid.

1. The Experimental Data

The solubility of hydrogen in metals has been most extensively measured for the metals in the first and second long periods of the Periodic Table. The variation of the hydrogen solubility with temperature at one atmosphere pressure for metals in the first long period is given in Fig. (2), that for metals in the second long period is in Fig. (3) and data for other metals is given in Fig. (4). The sources of the data are indicated in Table (2). The reference works of Smith[18] and Smithells[19] have been indicated repeatedly for metals where they give solubilities recalculated from original data, however these data points were not included in the computer analysis of the solubility data (next section).

The data in Figs. (2), (3), and (4) cover a wide range of solubilities; at 400° C the solubility of hydrogen in thorium is greater than that in aluminum by a factor of 10^8. For metals which dissolve only small amounts of hydrogen, changes in lattice parameter with hydrogen content are probably too small to be measurable. For metals which dissolve large amounts of hydrogen some data is available on changes of lattice parameter and the positions occupied by the H-atoms in the metal lattice. Shull, Rundle and Woolan[20] have shown that for zirconium and thorium there is little change in lattice parameter until appreciable amounts of hydrogen are absorbed and then there is a change in the lattice

VARIATION OF HYDROGEN SOLUBILITY IN
PERIOD IV METALS WITH TEMPERATURE
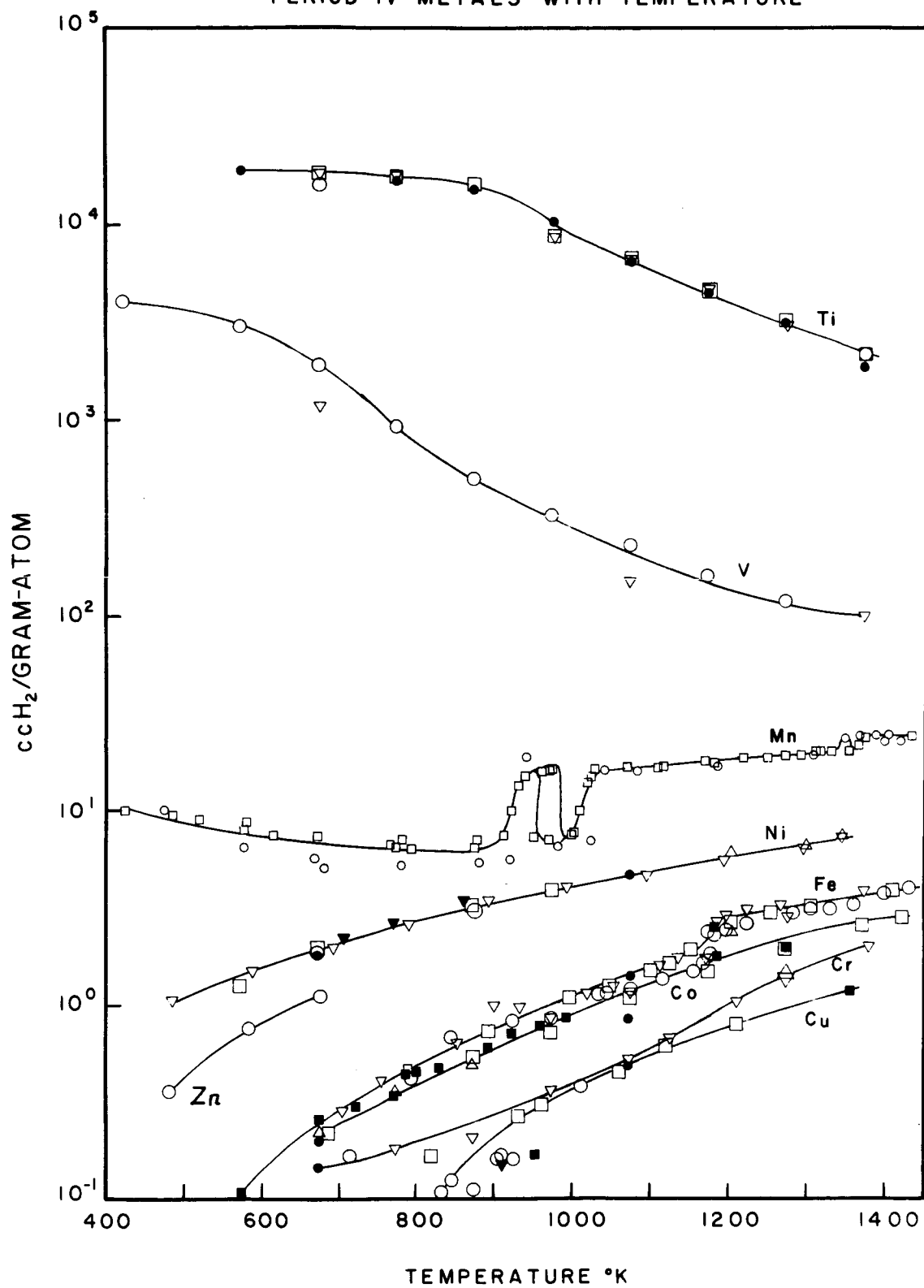
Fig. 2

VARIATION OF HYDROGEN SOLUBILITY IN
PERIOD V METALS WITH TEMPERATURE
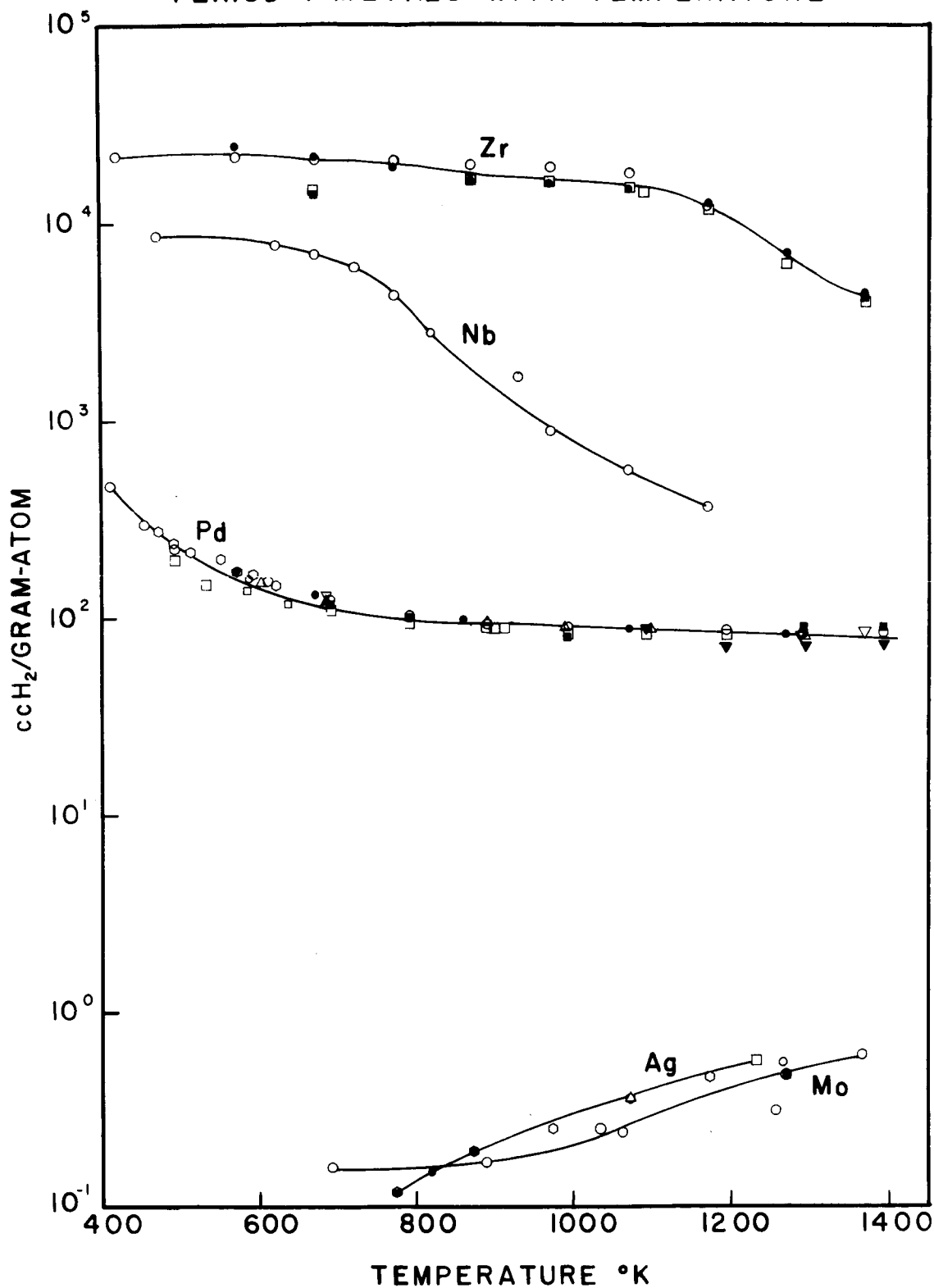
Fig. 3

VARIATION OF HYDROGEN SOLUBILITY IN
PERIOD VI AND VII METALS WITH TEMPERATURE
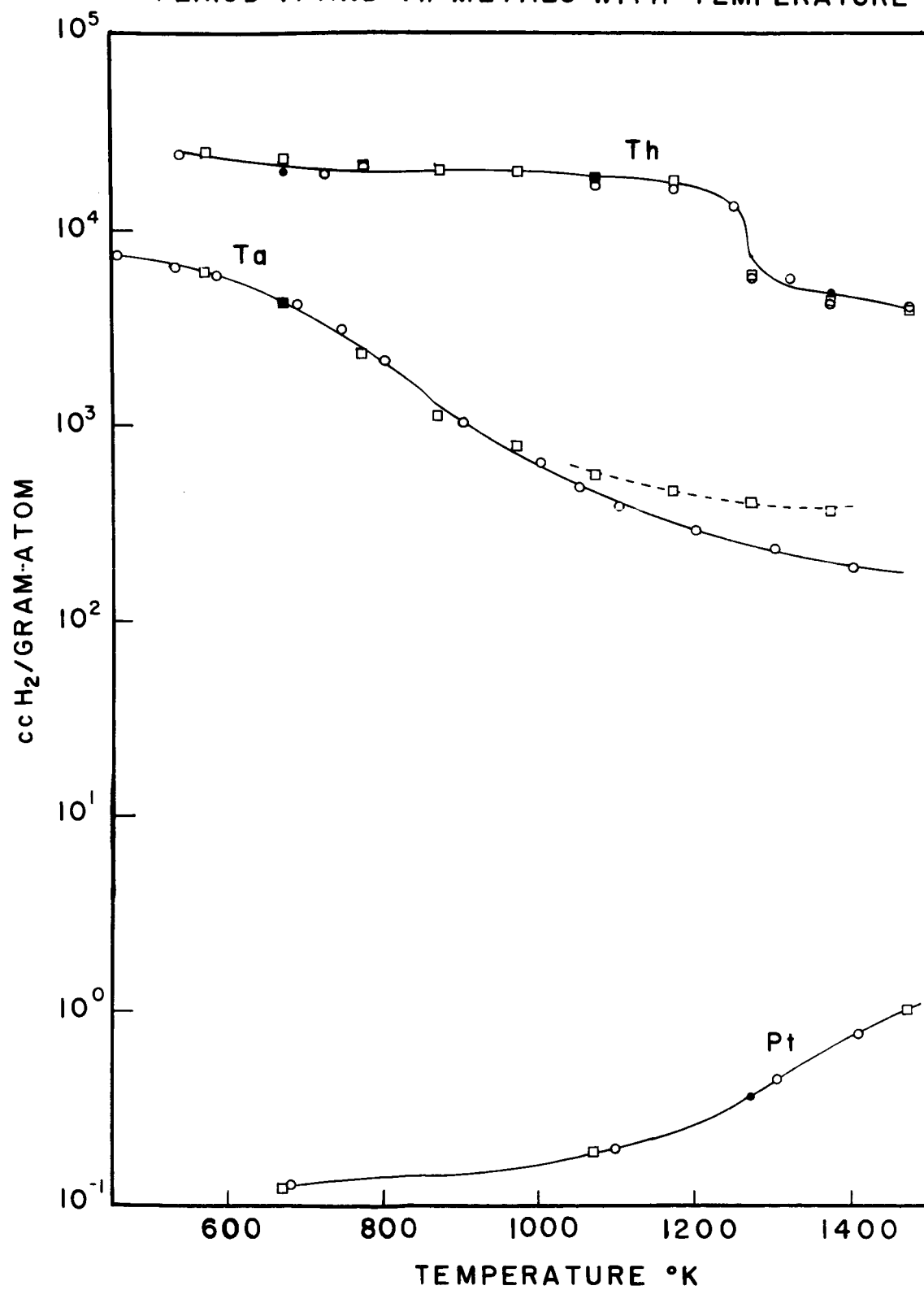
Fig. 4

TABLE 2

SOURCES OF THE HYDROGEN SOLUBILITY DATA

1

Al	○	C. E. Ransley and H. Neufeld, J. Inst. Metals. 74, 599 (1948).
	□	W. Eichenauer and A. Pebler, Z. Metallk. 48, 373 (1957).
	●	L. L. Bircumshaw, Trans. Faraday Soc. 31, 1439 (1935).
Ti	●	A. Sieverts, Z. Metallk. 21, 37 (1929).
	○	D. P. Smith, Hydrogen in Metals, (The University of Chicago Press, Chicago, 1948) - quoted from Sieverts.
	▽	L. Kirschfeld and A. Sieverts, Z. Phyik. Chem. 145A, 227 (1929).
	□	A. Sieverts, H. Huber, and L. Kirschfeld, Chem. Ber. 59, 2891 (1926).
V	△	D. P. Smith, loc. cit.
	○	L. Kirschfeld and A. Sieverts, Z. Elektrochem. 36, 123 (1930).
Cr	●	D. P. Smith, loc. cit.
	○	C. J. Smithells, Metals Reference Book, (Interscience Publishers, Inc., New York, 1955) 2nd ed pp. 535-536.
	▽	L. Luckemeyer-Hasse and H. Schenk, Arch. Eisenhüttenw. 6, 209 (1932).
Mn	○	A. Sieverts and H. Moritz, Z. Physik. Chem. 180A, 249 (1937).
	□	E. V. Potter and H. C. Lukens, Trans. AIME. 171, 401 (1947).
	●	C. J. Smithells, loc. cit.
Fe	●	D. P. Smith, loc. cit.
	○	E. Martin, Arch. Eisenhüttenw. 3, 407 (1929).
	□	A. Sieverts, Z. Physik. Chem. 77, 591 (1911).
	■	W. Eichenauer, H. Kunzig, and A. Pebler, Z. Metallk. 49, 220 (1958).
	▲	C. J. Smithells, loc. cit.
	△	A. Sieverts and W. Krumbhaar, Chem. Ber. 43, 893 (1910).
	▽	A. Sieverts, G. Zapf, and H. Moritz, Z. Physik. Chem. 183A, 19 (1938).
Co	●	D. P. Smith, loc. cit.
	■	C. J. Smithells, loc. cit.
	○	P. Beckmann, Dissertation, Leipzig. - quoted by A. Sieverts and H. Hagen: Z. Physik. Chem. 169, 237 (1934).
	□	A. Sieverts and H. Hagen, Z. Physik. Chem. 169, 237 (1934).
	△	W. Siegelin, K. H. Lieser, and H. Witte, Z. Elektrochem. 61, 359 (1957).
	▽	A. Sieverts, Z. Metallk. 21, 37 (1929).

Ni	●	D. P. Smith, loc. cit.
	■	C. J. Smithells, loc. cit.
	○	K. H. Lieser and G. Rinck, Z. Elektrochem. 61, 357 (1957).
	▼	W. Eichenauer, W. Loser, and H. Witte, Z. Metallk. 56, 287 (1965).
	□	K. H. Lieser and H. Witte, Z. Physik. Chem. 202, 321 (1954).
	△	A. Sieverts and W. Krumbhaar, Chem. Ber. 43, 893 (1910).
	▽	A. Sieverts, Z. Metallk. 21, 37 (1929).
Cu	●	C. J. Smithells, loc. cit.
	□	W. Himmler, Z. Physik. Chem. 195, 244 (1950).
	▼	W. Eichenauer, W. Löser and H. Witte: Z. Metallk. 56, 287 (1965).
	○	W. Eichenauer and A. Pebler, Z. Metallk. 48, 373 (1957).
	■	K. H. Lieser and H. Witte, Z. Physik. Chem. 202, 321 (1954).
Zn	○	K. Iwase, Sci. Rept. Tokohu Univ. First Ser. 15, 531 (1926).
Zr	●	C. J. Smithells, Gases and Metals, (Chapman and Hall, Ltd., London, 1937) pp. 161.
	○	M. N. A. Hall, S. L. H. Martin, and A. L. G. Rees, Trans. Faraday Soc. 41, 306 (1945).
	□	A. Sieverts and H. Moritz, Z. Anorg. Allgem. Chem. 247, 124 (1941).
	■	D. P. Smith, loc. cit.
Nb	○	A. Sieverts and H. Moritz, Z. Anorg. Allgem. Chem. 247, 124 (1941).
Mo	■	C. J. Smithells, Metals Reference Book, (Interscience Publishers, Inc., New York, 1955) 2nd ed. pp. 535-536.
	○	A. Sieverts and K. Bruning, Arch. Eisenhüttenw. 7, 641 (1934).
Pd	●	A. Sieverts and G. Zapf, Z. Physik. Chem. 174A, 359 (1935).
	○	A. Sieverts, Z. Physik. Chem. 88, 103 (1914).
	□	J. Hagenacker, Dissertation, Leipzig, 1909. - quoted by A. Sieverts, Z. Physik. Chem. 88, 103 (1914).
	■	F. Müller, Dissertation, Leipzig, 1911. - quoted by A. Sieverts, Z. Physik. Chem., 88, 103 (1914).
	△	E. Jurisch, Dissertation, Leipzig, 1912. - quoted by A. Sieverts, Z. Physik. Chem. 88, 103 (1914).
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structure when the compounds ZrH and ThH are formed. They showed that these compounds are body-centered tetragonal and, by neutron diffraction, that the hydrogen atoms are situated at the center of tetrahedrons of metal atoms. Woolan, Cable, and Koehler[21] showed by neutron diffraction that the H atoms occupy octahedral sites in F.C.C. Ni.

This work deals only with hydrogen-metal solutions in equilibrium with gaseous hydrogen. It is however possible to surcharge a metal by making it cathode in an electrolytic cell, especially if the metal surface is coated with certain catalysts. Occlusion of ten times the amount of hydrogen dissolved in the metal in equilibrium with gaseous hydrogen at 1 atmos. pressure can occur and this may damage the structure of the metal and even produce large blisters on the surface. The surcharged hydrogen alloys are not stable and the hydrogen is occluded in rifts; the pockets of hydrogen responsible for the formation of blisters undoubtedly contain molecular hydrogen.

Although the occlusive capacity of a metal in cathodic surcharging can be greatly increased by cold-working, the equilibrium solubility is not changed thus. Carmichael, Hornady, Morris and Parlee[22] have shown that α-iron has the same hydrogen solubility in the well-annealed state as it has after being cold worked by 75% and annealed for a short time at 430° C. At this annealing temperature the greater part of the cold-worked hardness remains and there is no microscopically visible recrystallization.

It may have been supposed that the degree of cold-working would affect the hydrogen solubility by increasing the number of dislocations in the metal and thus providing low energy sites for the hydrogen atoms. However, it can easily be shown that this effect is not important at

temperatures above which the hydrogen solubility of most metals can be measured. For B.C.C. α-iron the dislocations lie along (110) - planes and according to the measurements of Nutting and Brandon[23] there are 10^{10} dislocations cutting an area of 1 cm^2. in heavily cold-worked iron. This infers that the number of dislocation sites per cm^2. is 5 x 10^{17}. At 500° C iron dissolves 40 x 10^{17} hydrogen atoms per cm^3.; thus even at low temperatures in heavily cold-worked metal there are many more hydrogen atoms than dislocation sites.

2. Models for Hydrogen-Metal Solutions

A model for hydrogen-metal solutions was proposed by Fowler and Smithells[24] for those metals whose H-solubility is small (Cu, Ni, Fe, Co) in which the H-atoms dissolve as protons and have translational freedom in a large fraction f of the volume of the metal. The chemical potential μ_H^S of a proton in the solid can be then written in the form

$$\mu_H^S = E_o + kT \ln \frac{h^3}{(2\pi mkT)^{3/2}} + kT \ln \frac{P_{H_2}}{kTf} \tag{19}$$

where E_o is the energy of an H-atom at rest in the solution with respect to an H-atom at rest in a vacuum. Equating this μ_H^S to the chemical potential μ_H^S in the gas yields the solubility equation,

$$\frac{\rho \theta T^{1/4}}{M P_{H_2}^{1/2}} = \frac{1}{N_o} \frac{(2\pi mk)^{3/2}}{h^3} \left\{ \frac{h^3}{(2\pi 2mk)^{3/2}} \cdot \frac{2h^2}{8\pi^2 I_{H_2} k} \frac{1}{k} \right\}^{1/2} f \ x$$

$$x \ e^{-(E_o - \frac{1}{2} E_{H_2}^o)/kT} \tag{20}$$

where ρ is the density of the metal and M its atomic weight.

There is however a serious objection to the translational model since it predicts diffusion coefficients for the diffusion of hydrogen through the metal lattice which are much higher than the measured values. In this model the diffusion of hydrogen through the metal is analagous to the Knudsen flow of gas molecules at low pressure through a tube whose radius g is small compared to the mean free path of the gas molecules. The diffusion coefficient for such a flow is proportional to $g\bar{v}$, where $\bar{v}$ is the mean velocity of the molecules[25], so that: -

$$D = K'g\left(\frac{RT}{M_H}\right)^{1/2} \tag{21}$$

M_H is the molecular weight of the gas and the coefficient K' is close to unity. Putting $g = 10^{-8}$ cm, $D = 1.52 \times 10^{-3}$ cm^2/sec at 500° K. The ratio of this calculated D to the smallest observed D (for α-iron) at 500° K is 2.7 x 10'.

For copper ($f = 0.8$) equation (20) gives reasonably good agreement with the measured solubility data but for other metals the agreement is poor.

Fowler and Smithells[24] also deduced a solubility equation for the hydride-forming metals by assuming that the H-atoms mix randomly in the metal lattice, do not perturb its vibrational spectrum, and do not interact. It was assumed also that the vibrations of the dissolved H-atoms were not excited in the temperature range considered. It was shown that despite these radical assumptions the general shape of the solubility isobars could be explained by the model.

Lacher[26] gave a theoretical treatment of Pd-H solutions in which the partial energy $\bar{E}_u$ is proportional to the fraction of filled sites but the configurational entropy is ideal. The model was qualita-

tively successful in predicting a critical temperature for concen-
trated Pd - H alloys below which two solid phases exist.

Eichenauer[27] has presented a theoretical discussion of
the solubility and diffusivity of hydrogen in metals where the solu-
bility is low. He calculated the vibrational frequency of a H-atom
in solution from the solubility data using a quasi-regular solution
model for the solid. It was shown that these calculated frequencies
were in reasonably good agreement with those calculated from the acti-
vation energy for the diffusion of H-atoms through the metal lattice
using a diffusion model due to Wert and Zener[28] in which the H-atoms
vibrate in a parabolic potential well in their lattice sites and the
potential energy between adjacent sites varies sinusoidally.

3. The Quasi-regular Model applied to Hydrogen-Metal Solutions

In this work it is assumed that the H-atoms in solution are
bound at interstitial sites and execute many vibrations before jumping
into an adjacent site; in other words the activation energy for diffusion
is appreciably greater than the mean vibrational energy of an H-atom.
A graphical representation of the model is given in Fig. (5). The
dissociation energy of an H_2 - molecule is $-E^o_{H_2}$. The difference in
energy between an H-atom in the gas and an H-atom in the solid is
$\bar{E}_u$ and the enthalpy of solution of H_2 - molecules per atom is

$$\Delta H = \bar{E}_u - \frac{1}{2} E^o_{H_2} - \frac{7}{4} kT . \tag{22}$$

It can be seen that previous classification of H-metal solutions into
endothermic and exothermic occluders does not reflect a fundamental
difference in the solutions since H-atoms are always absorbed with the
evaluation of energy $\bar{E}_u$ and the sign of ΔH depends on whether $\bar{E}_u$ is
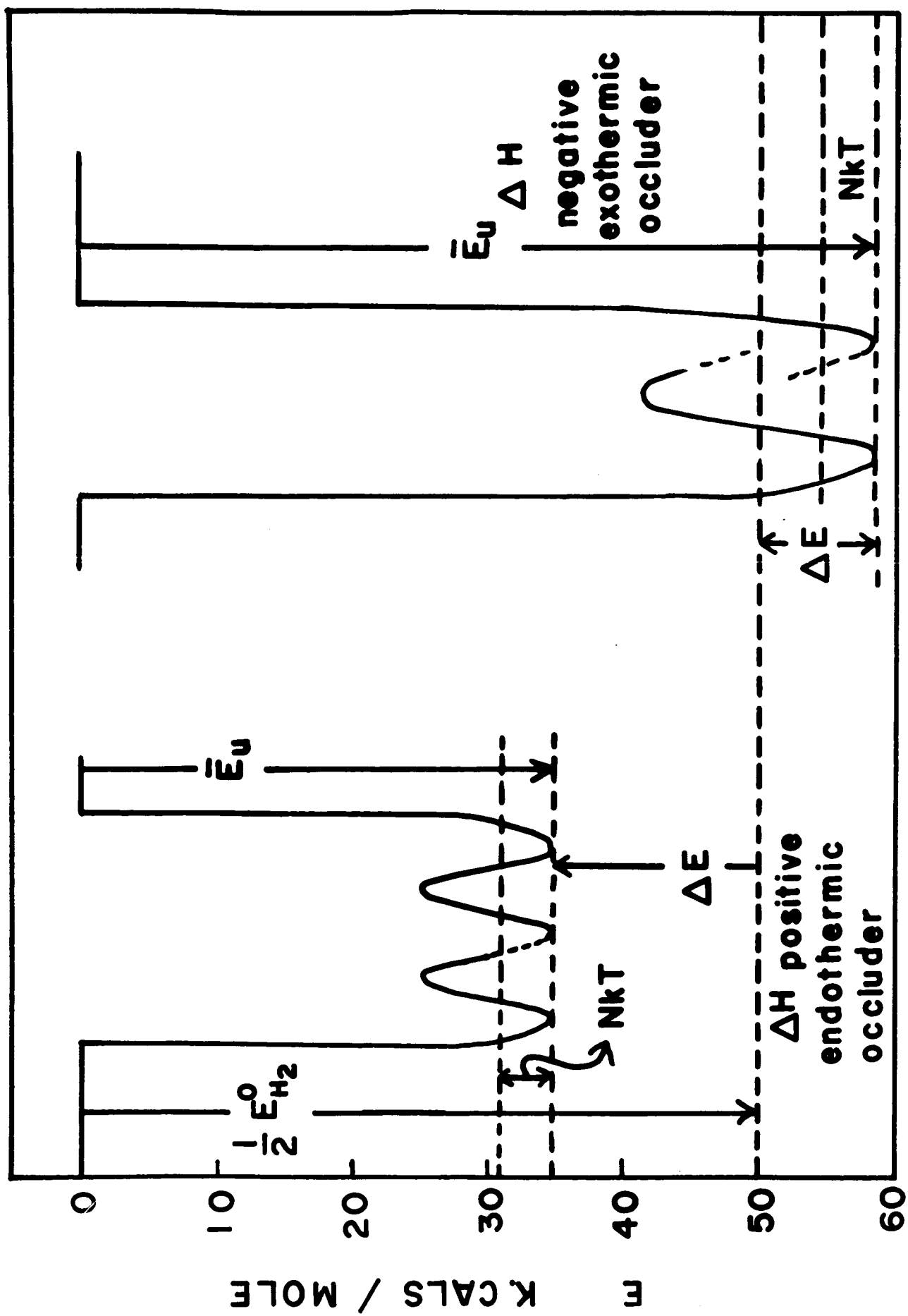greater or less than $\frac{1}{2} E^o_{H_2}$.

Fig. 5

The treatment of the H-metal solutions is parallel to that of N in iron and the chemical potential of an H-atom in solution is given by equation (2) and the solubility equation is given by replacing N with H in equations (14) and (15). For the temperature range involved $Z_{H_2}^V$ is essentially unity. It was assumed that the octahedral interstices were occupied so that $\beta = 1$ for F.C.C. lattices and $\beta = 3$ for B.C.C. lattices and for the complex α and γ - Mn structures the value of β has been taken as 3.

Plots of $\ln[(\theta/\beta)/(1-\theta/\beta)][T^{7/4}/P_{H_2}^{1/2}]$ vs $1/T$ will have a slope given by $-(\bar{E}_u - \frac{1}{2}E_{H_2}^o)/k$ and an intercept given by $\ln \lambda + \bar{S}_u^V/k$. These plots are shown in figs. (6), (7), and (8) corresponding to the solubility data given in Figs. (2), (3), and (4). It is to be noted that with the exceptions of Ni and Pt the plots are good straight lines. A computer was used to find the best values of the slopes and intercepts of the plots of figs (6), (7), and (8) using the method of least squares and the values of the partial energy $\bar{E}_u$ and excess partial entropy $\bar{S}_u^V$ of H-atoms in the solutions is presented in table (3). For the solvents Th, Zr, and Mo the temperature range covered by the data in the one-phase alloys is so small that no reliance can be placed on the values of $\bar{E}_u$ and $\bar{S}_u^V$.

4. Thermodynamic Parameters of Hydrogen-Metal Solutions

Table 3 is set out with the metals arranged in the form of the Periodic Table. Immediately below each solvent metal is given the value of $\bar{S}_u^V/k$ and then the value of $-\bar{E}_u$ in k. cals/mole.

It can be seen that in all the periods the energy of solution increases (becomes less negative) from left to right; the only exception

Fig. 6

Fig. 7

Fig. 8

TABLE 3

Values of $\bar{S}_u^v/k$ and $-\bar{E}_u$

Al°
1.69
37.8

Ti*	V+	Cr+	α-Mn	γ-Mn	α-Fe+	γ-Fe°	Co°	Ni°	Cu°	Zn*	Ga
2.10	1.31	5.30	0.39	3.80	2.53	5.17	4.26		5.21	2.64	
65.7	55.9	32.9	50.9	45.0	42.5	39.8	41.1		36.9	45.9	

Zr*	Nb+	Mo+
0.24	0.46	0.14
73.5	59.8	44.6

Pd°	Ag°
	2.45
	42.3

Th°
5.35
60.1

Ta+
1.74
56.8

Pt°
6.06
32.9

° F.C.C.

+ B.C.C.

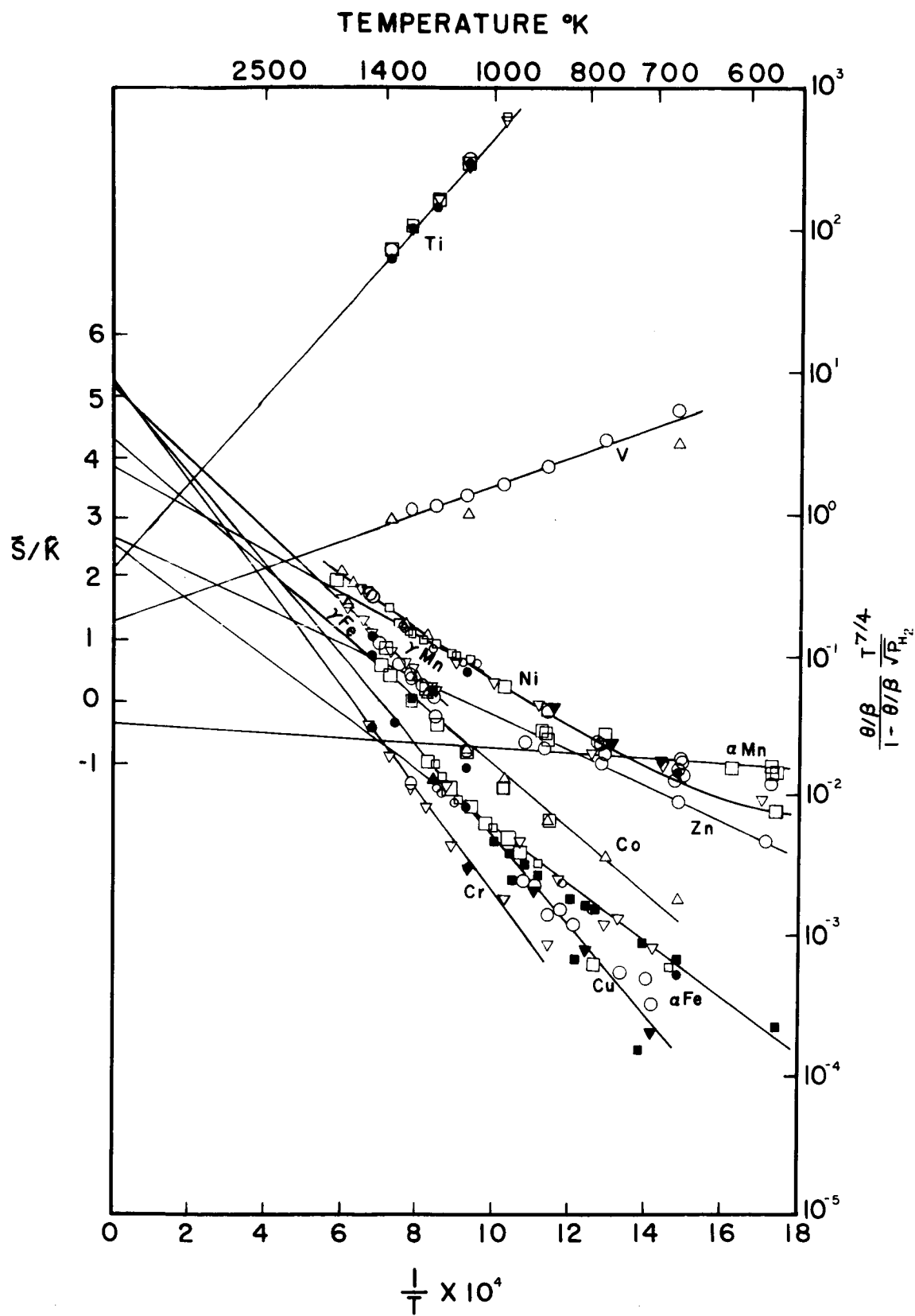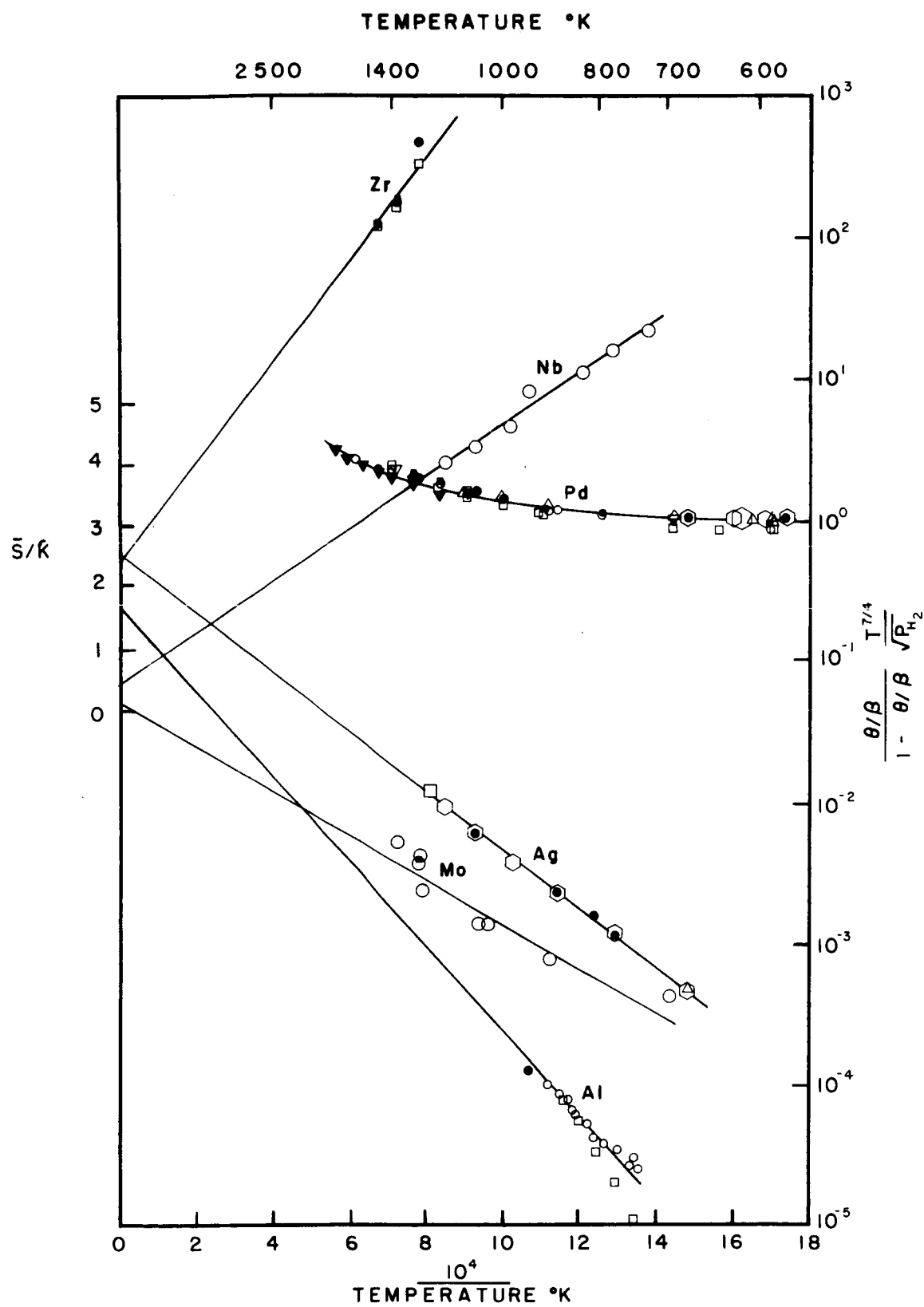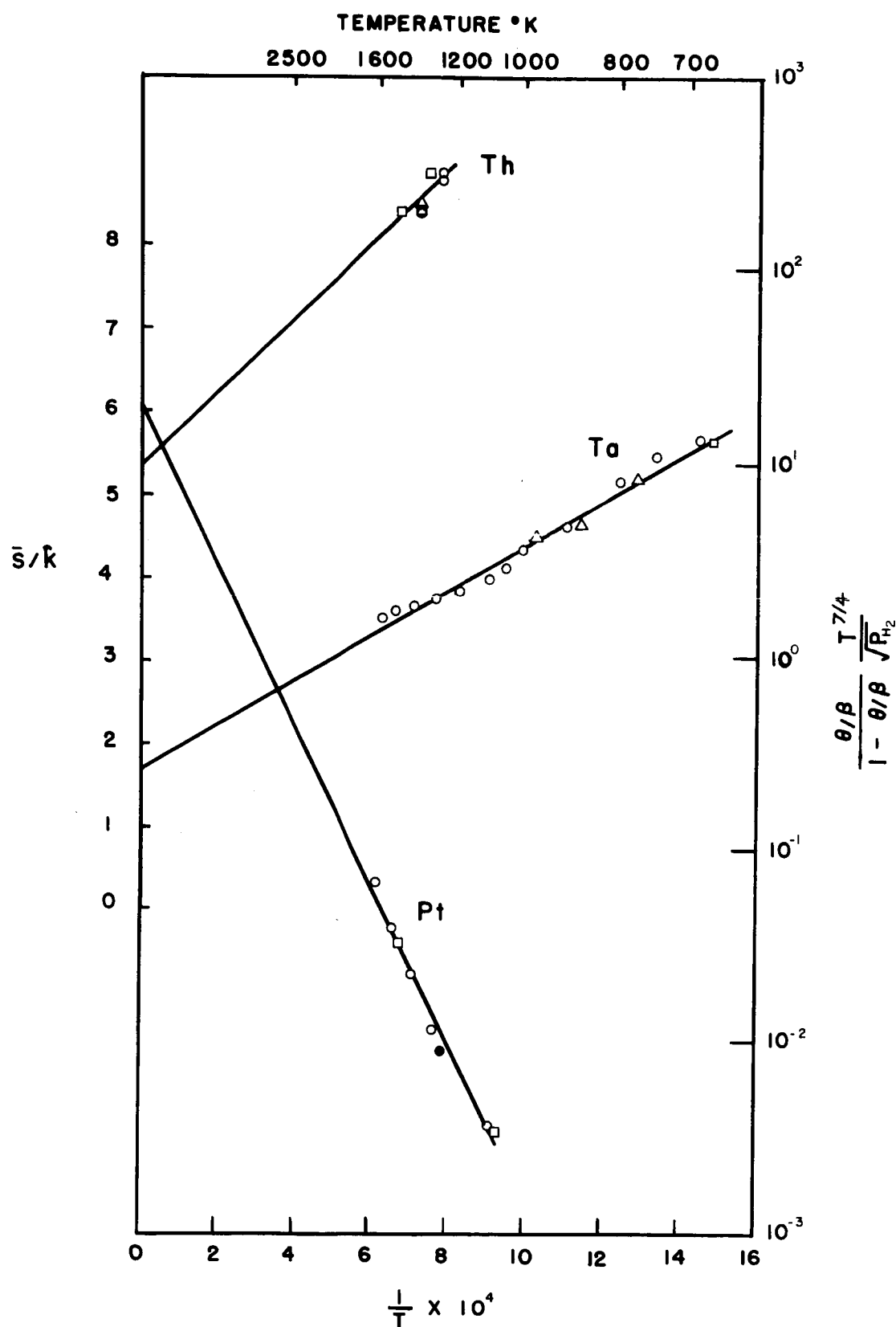* C.P.H.

being Cr in the first long period where the energy of solution of an

H-atom is anomalously high. In view of the curvature no data has been

given for Ni but the best value for $\bar{E}_u$ is 45.0 k. cals/mole.

In the second long period the $\bar{E}_u$ - values increase regularly from

Zr → Nb → Mo and there is also a regular increase in the first long period

until Cr and then $\bar{E}_u$ changes only slightly from γ-Mn to Ni. This con-

stancy of $\bar{E}_u$ may be a reflection of the mechanism of solution. Franck[29]

suggested that if hydrogen dissolves in metals in the form of a proton

then the heat of solution can be written

$$\bar{E}_u = I_u - W_F + \bar{E}_p \qquad (23)$$

where I_u is the ionization energy of H, $\bar{E}_p$ is the heat of solution of

a proton, and W_F is the thermionic work function of the metal solvent.

If it is assumed that amongst these transition metals $\bar{E}_p$ does not vary

much then $\bar{E}_u + W_F$ should be constant. For Co, Ni, and α-Fe the values

of $\bar{E}_u + W_F$ are 60.55, 61.26, and 60.76 k. cals/mole respectively but for

Cr, $\bar{E}_u + W_F$ is 73.13 k. cals/mole. Although there is good evidence

from measurements of magnetic susceptibilities in the Pd-H system that

H is ionized in Pd with the extra electrons from the H entering the holes

in the d-band, the data for W_F is too scant to allow any further persual

of the ideas underlying equation (23).

There seems to be little correlation between the position of the

solvent elements in the Periodic Table and the value of $\bar{S}_u^v/k$. In general

the solutions with the lowest (most negative) heats of solution have

smaller partial excess entropies which would be expected since the more

tightly bound protons would vibrate with a higher frequency and give rise

to a smaller vibrational entropy. If it is assumed that $\bar{S}_u^v$ arises only

from uncoupled vibrations of the solute atoms, their Einstein frequency ν can be calculated from the equation,

$$\overline{S}^V_u = 3k\left\{\frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln\left(1 - e^{-h\nu/kT}\right)\right\} . \qquad (24)$$

Values of ν calculated from this formula for $T = 1000°$ K enable values for the activation energy E_D for the diffusion of hydrogen through the solvent metals to be estimated from the model of Wert and Zener[28]. The values of E_D are all of the right order of magnitude but show no systematic agreement with experimental values of E_D. Such a simple interpretation of the $\overline{S}^V_u$ data is almost certainly invalidated by the neglect of the lattice contribution to the excess entropy and the neglect of the change in electronic specific heat and the uncoupling of electron spins which may occur when the extra electron enters the Fermi energy levels of the solvent metal.

D. CONCLUSIONS

The work presented in this report involves the analysis of data for the equilibrium between gaseous phases and very dilute interstitial solid solutions in order to derive the useful thermodynamic parameters of solute atoms which are essentially isolated in a solvent matrix. The method used does not involve using extraneous data for equilibriums with the phase defining a standard state and the data have been presented as partial quantities instead of the more usual relative partial quantities.

The energy data have proved useful in discussing problems connected with the solubility of Fe_3C in ferrite[15] and the diffusion of C through ferrite[17]. The partial energy of solution of hydrogen in metals has been shown to depend in a fairly regular fashion on the position of the solvent metal in the Periodic Table.

The excess entropies deduced for Ag-O and Fe-N solutions[5] have been interpreted as vibrational entropies and their magnitude can be explained[5] by a simple model in which the entropy change due to the shear and dilational strains in the matrix concomitant with the insertion of a solute atom[30]. The $\bar{S}_u^v$ data for hydrogen alloys are not easy to interpret since it is probable that electronic specific heat changes make a large contribution to the excess entropy.

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